

NATIONAL BUREAU OF STANDARDS REPORT

9918

Progress Report

on

HYDRATED CALCIUM AND CALCIUM-SODIUM CARBONATES



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards¹ provides measurement and technical information services essential to the efficiency and effectiveness of the work of the Nation's scientists and engineers. The Bureau serves also as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To accomplish this mission, the Bureau is organized into three institutes covering broad program areas of research and services:

THE INSTITUTE FOR BASIC STANDARDS . . . provides the central basis within the United States for a complete and consistent system of physical measurements, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. This Institute comprises a series of divisions, each serving a classical subject matter area:

—Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Physical Chemistry—Radiation Physics—Laboratory Astrophysics²—Radio Standards Laboratory,² which includes Radio Standards Physics and Radio Standards Engineering—Office of Standard Reference Data.

THE INSTITUTE FOR MATERIALS RESEARCH . . . conducts materials research and provides associated materials services including mainly reference materials and data on the properties of materials. Beyond its direct interest to the Nation's scientists and engineers, this Institute yields services which are essential to the advancement of technology in industry and commerce. This Institute is organized primarily by technical fields:

—Analytical Chemistry—Metallurgy—Reactor Radiations—Polymers—Inorganic Materials—Cryogenics²—Office of Standard Reference Materials.

THE INSTITUTE FOR APPLIED TECHNOLOGY . . . provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government. The principal elements of this Institute are:

—Building Research—Electronic Instrumentation—Technical Analysis—Center for Computer Sciences and Technology—Textile and Apparel Technology Center—Office of Weights and Measures—Office of Engineering Standards Services—Office of Invention and Innovation—Office of Vehicle Systems Research—Clearinghouse for Federal Scientific and Technical Information³—Materials Evaluation Laboratory—NBS/GSA Testing Laboratory.

¹ Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

² Located at Boulder, Colorado, 80302.

³ Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

311.05-11-3110561

June 30, 1968

NBS REPORT

9918

Progress Report

on

HYDRATED CALCIUM AND CALCIUM-SODIUM CARBONATES

By

Walter E. Brown* and Brian Dickens**

* Director, Research Associate Program of the American Dental Assoc., Dental Research Section, National Bureau of Standards, Washington, D. C. 20234

** Research Chemist, Dental Research Section, National Bureau of Standards, Washington, D. C. 20234

This investigation was supported in part by Research Grant DE-00572 to the American Dental Association from the National Institute of Dental Research, and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association; the National Institute of Dental Research; the Army Dental Corps; the Dental Sciences Division, School of Aerospace Medicine, USAF; and the Veterans Administration.

IMPORTANT NOTICE

NATIONAL BUREAU OF STANDARDS
for use within the Government. It is not to be distributed outside the Government without the express written permission of the Director of the National Bureau of Standards, Washington, D. C. The Report has been specifically prepared for use within the Government. It is not to be distributed outside the Government without the express written permission of the Director of the National Bureau of Standards, Washington, D. C. The Report has been specifically prepared

Approved for public release by the Director of the National Institute of Standards and Technology (NIST) on October 9, 2015

accounting documents intended for use within the Government. It is not to be distributed outside the Government without the express written permission of the Director of the National Bureau of Standards, Washington, D. C. The Report has been specifically prepared for use within the Government. It is not to be distributed outside the Government without the express written permission of the Director of the National Bureau of Standards, Washington, D. C. The Report has been specifically prepared



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS



HYDRATED CALCIUM AND CALCIUM-SODIUM CARBONATES

Abstract

Crystallographic properties of two hydrated calcium carbonates, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, are described. Hydrated salts are of potential importance in the nucleation and crystal growth of anhydrous salts, both in vitro and in vivo, because of interfacial energy, kinetics, growth poisons, and epitaxy. $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ has four formula weights in a cell $\underline{a} = 8.87 \pm .02$, $\underline{b} = 8.23 \pm .01$, $\underline{c} = 11.02 \pm .02\text{\AA}$, and $\underline{\beta} = 110.2 \pm .1^\circ$, with space group $\text{C}2/\text{c}$. $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ (gypsum) has four formula weights in a cell $\underline{a} = 14.36 \pm .002$, $\underline{b} = 7.781 \pm .001$, $\underline{c} = 11.209 \pm .002\text{\AA}$, $\underline{\beta} = 127.84 \pm .01^\circ$, also with space group $\text{C}2/\text{c}$. The structure of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ contains $\text{Ca}-\text{CO}_3$ ion pairs isolated from each other by water molecules. The decreases in volume associated with the formation of hydrated salts from the corresponding anhydrous salts and liquid water suggest that hydrated salts may be the stable forms under high hydrostatic pressure. In the ocean deeps, the high pressures and low temperatures favor formation of the hydrated calcium carbonates.

Text

The possible importance of hydrated calcium phosphates and carbonates in biological mineralization is not adequately recognized. In calcium carbonate mineralization, nearly all of the attention has been given to the anhydrous salts calcite, aragonite and vaterite, which are known to occur both simultaneously and individually in the shells of molluscs¹ and in other biological minerals,² including gallstones.³ We report here on the crystallographic properties of two hydrated calcium carbonates, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, which may act as precursors to the formation of other salts in aqueous environments.

For reasons given below, a variety of conditions may facilitate formation of the hydrated calcium carbonates, rather than the anhydrous salts, and thus allow them to participate in biological mineralization at least as precursors. The two known hydrated calcium carbonates, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ^{4,5} and $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ ^{5,6}, have been neglected in this respect, possibly because of their metastability with respect to the anhydrous salts. The salts gaylussite,⁷ $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, and pirssonite,⁸ $\text{CaNa}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, may also be important because they are hydrated and because they contain sodium, a common constituent of mineralization media.

The conditions under which biological mineralizations occur require the following four factors to be taken into account.

1. Surface energy: During nucleation and early states of crystal growth, the interfacial energy is a dominant factor in controlling the stability of the particles. Measured against a vacuum, the surface energy relates to the asymmetry of the attractive forces on the outermost ions so that the surface energy tends to be high when the forces between ions are large. In hydrated salts some of the strong electrostatic attractive forces are reduced by intervening water molecules, and therefore the surface energy of a hydrated salt should be less than that of an anhydrous salt. Furthermore, water molecules in the nucleus or crystallite reduce the difference in composition between it and the aqueous environment because the hydrogen bonding within the crystal can extend to the liquid to increase the compatibility of the two phases. The aqueous environment

in effect decreases the asymmetry of the attractive forces around the ions on the particle surface. Thus, in the early stages of growth, hydrated species should be favored over anhydrous species because of their probably lower interfacial energy.

2. Kinetic factors: In many instances, hydrated salts crystallize more rapidly than their anhydrous counterparts. For example, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ are frequently formed under conditions where CaHPO_4 or $\text{Ca}_5\text{OH}(\text{PO}_4)_3$ is the stable salt thermodynamically⁹. Other things being equal, this tendency should be greatest for small cations of multiple valence (i.e., those with negative entropies of dissolution). From this point of view, when rate is an important consideration, formation of the hydrated calcium carbonates should be favored over the anhydrous salts.

3. Crystal-growth poisons: Polyphosphates⁵, magnesium⁶ and concentrated sugar solutions¹⁰ all apparently repress the growth of anhydrous calcium carbonates, and thus permit the formation by default of the hydrated salts. Since magnesium, polyphosphates and sugars are present in biological fluids, they may inhibit formation of nuclei of the anhydrous calcium carbonates in vivo and permit their growth perhaps epitaxially or by subsequent rearrangement in the nucleus once it has attained a critical size for the anhydrous salt.

4. Epitaxy and heterogeneous nucleation: Most nucleation processes are thought to be heterogeneous rather than homogeneous. It is widely believed, for example, that in tooth and bone, collagen and other proteins participate in the formation of the crystallites by reducing their surface energies through epitaxy or heterogeneous nucleation. The same presumably applies to calcium carbonate mineralization. Because of their hydrophilic nature, the proteins present at the site of in vivo

calcium carbonate mineralization should reduce the energy of heterogeneous nucleation of a hydrated form to a lower value than that of an anhydrous form.

If a hydrated form acts as a precursor to an anhydrous salt, it could control the identity, morphology and crystal orientation of the product through epitaxy or topotaxy. Thus it is important to know the structural details of hydrated salts of potential biological significance. We have determined the crystal structures of two hydrated carbonates; some of their important features are reported below.

Good crystals of $\text{CaNa}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ were obtained from a gel of calcium carbonate in the presence of sodium polyphosphate and excess sodium carbonate^{5,11}. The unit cell^{*} at room temperature was found to be $a = 14.361 \pm .002$, $b = 7.781 \pm .001$, $c = 11.209 \pm .002\text{A}$, and $\beta = 127.84 \pm .01^\circ$. The calculated density, 1.99 g/ml, assuming four formula weights per unit cell, is the same as the reported⁷ density. The extinctions $h+k = 2n+1$ for hkl , and $l = 2n+1$ for hol lead to the possible space groups $C2/c$ and Cc . The crystal morphology contains a center of symmetry, suggesting the

*The uncertainties quoted on cell dimensions are estimates based on experience with the technique used for measurement. In the authors' opinion a conservative estimate of error will be obtained if these uncertainties are treated as standard deviations.

centro-symmetric space group C2/c which has been confirmed by a determination of the crystal structure. An important feature of the structure^{1,2} is the presence of CO_3 -Ca- CO_3 ion triplets, each of which is isolated from other such ion triplets by water molecules and sodium ions.

Large tablets and rods (1-2 mm in diameter) of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ were grown from a calcium carbonate gel after the manner of Brooks, Clark and Thurston⁵. Under the microscope, two distinct views were common: (1) Plates with low birefringence and parallel extinction. These, when modified by $\{110\}$ -type faces, exhibited $2/m$ symmetry, with symmetrical extinction, and the fast direction, N_β , parallel to b; the trace of the $\{110\} \wedge \{110\}$, 93.4° , yielded an axial ratio $\underline{a}/\underline{b} = 1.05$; (2) Short, highly birefringent (010) rods or plates with the slow direction, N_γ , extinguishing at 17° from c in acute β; these yielded β = 109.4° and $\underline{c}/\underline{a} = 1.28$.

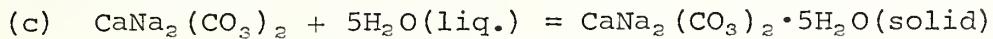
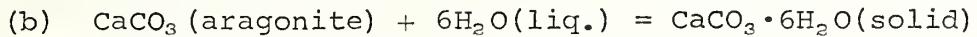
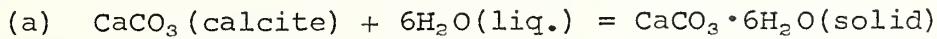
The cell constants* were determined to be $\underline{a} = 8.87 \pm 0.02$, $\underline{b} = 8.25 \pm .01$, $\underline{c} = 11.02 \pm .02\text{\AA}$, and $\underline{\beta} = 110.2 \pm .1^\circ$ at -120°C using a Weissenberg camera modified to bathe the crystal continuously in a stream of cold gaseous nitrogen. A superimposed aluminum powder pattern taken at room

*See footnote, previous page.

temperature was used as a standard. The calculated density of 1.80 g/ml, assuming four formula weights per unit cell, compares well with the reported^{1,3} density of 1.82 g/ml. The extinctions $h+k = 2n+1$ for hkl and $l = 2n+1$ for hol lead to the possible space groups $C2/c$ and Cc . The morphology of the crystals reveals a center of symmetry consistent with the centro-symmetric space group $C2/c$. The crystal structure has been determined from three-dimensional x-ray data.

The outstanding feature in the structure^{1,2} is the presence of isolated $\text{Ca}-\text{CO}_3$ ion pairs, each surrounded by water molecules. This is the first instance, to our knowledge, of the existence of this ion pair in a crystalline lattice, and should provide valuable insight into its structure and its relationship with the water environment. The $\text{Ca}-\text{CO}_3$ ion pair may have a significant concentration in solutions saturated with respect to calcium carbonates^{1,4}. Its lack of ionic charge suggests that it may play an important role in diffusion through membranes in the same way that has been suggested for $\text{Ca}-\text{SO}_4$ ion pairs^{1,5}.

At atmospheric pressure, the reactions



would be accompanied by 20, 18 and 13 percent decreases in volume, respectively, suggesting that at high hydrostatic pressures (such as those that occur in the abyssal layer of the oceans or in hydrostatic vessels) $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ in particular, and hydrated salts in general may be the most stable forms.

It is noteworthy in this connection that most deep sea animals have little or no calcereous materials in their skeletons¹⁶ and that CaCO_3 is essentially absent from sediments collected at depths greater than 5000 m¹⁷, presumably because of its increased solubility¹⁸. It has been suggested from electron microscopic examination of deep sea sediments that almost all the calcium carbonate is of organic origin¹⁹. However, the possibility must be considered that at great depths the calcium carbonates may have been converted in part into hydrated forms which rapidly decompose at normal temperatures and pressures (i.e., during sample recovery).

The participation of hydrated forms in nucleation should be a fairly general phenomenon. The formation of hydrated salts from their anhydrous counterparts and liquid water will usually involve a reduction in total volume. Therefore, a study of the nucleation of any salt, to be complete, should include a search for possible hydrated precursors under high hydrostatic pressures and low temperatures.

References

1. K. M. Wilbur, Chap. 8, "Shell Formation and Regeneration", in *Physiology of Mollusca*, K. M. Wilbur and C. M. Yonge, Eds., Vol. 1, Academic Press, New York (1964), and references therein.
2. T. Pobeguin, *Ann. Des Sc. Nat., Bot.*, 15, 29 (1954).
3. D. J. Sutor and S. E. Wooley, *Science*, 159, 1113 (1968) and references therein.
4. J. Johnston, H. E. Merwin and E. D. Williamson, *Amer. J. Sci.*, 41, 473 (1916).
5. R. Brooks, L. M. Clark and E. F. Thurston, *Phil. Trans. Roy. Soc.* A243, 145 (1951) and references therein.
6. F. Lippmann, *Naturwissen*, 46, 553 (1959).
7. C. Palache, H. Berman and C. Frondel, *Dana's System of Mineralogy*, 7th Ed., Vol. II, Wiley (1951) p. 234.
8. Reference 7, p. 232.
9. W. E. Brown, *Clin. Orth.*, 44, 205, (1966).
10. J. E. Mackenzie, *J. Chem. Soc.*, 123, 2409 (1923).

11. C. R. Bury and R. Redd, J. Chem. Soc., 1160 (1933).
12. B. Dickens and W. E. Brown, in preparation.
13. J. Hume and B. Topley, J. Chem. Soc., 2932 (1926).
14. W. F. Neuman, P. E. Morrow, T. Y. Toribara, L. J. Casarett, B. J. Mylryan and H. C. Hodge, J. Biol. Chem., 219, 551 (1956).
15. M. Walser, Amer. J. Physiol., 200, 1099 (1961).
16. H. U. Sverdrup, M. W. Johnson and R. H. Fleming, "The Oceans", p. 808, 853, Prentice-Hall (1942).
17. G. Arrhenius in "The Sea", M. N. Hill, Ed., 3, p. 689, 691, Interscience (1963).
18. B. C. Heezen and A. S. Laughton, reference 17, p. 347.
19. W. R. Rideal, reference 17, p. 869.

